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Mechanism of the process of photochemical metallization of dielectric surfaces

The possibility of applying copper-containing films on the surfaces of various samples was investigated in the paper. Flat and smooth copper plates and fabric were used for the study. The sample of dielectric material was immersed in the solution, then they were dried in the sun, and work was done on the deposition of copper on the surface of the sample. The study of the rate of photochemical reduction of copper showed that the process consisted of two stages. In the first 30 minutes of the first stage, by increasing the concentration of Halogens during drying of the coating, a semiconductor layer is formed, and in the second — the direct photochemical reduction of copper, which takes about 30 minutes, but then gradually slows down. At the second stage, the rate of the photochemical reaction is equal to the rate of chemical or galvanic metallization. As a result of the photochemical reaction, when drying the sorption layer under the influence of sunlight, copper semiconductors are formed, which shape metallic coatings on the surface. This, in turn, can be used to make thinner films.

Keywords: mechanism, photochemistry, metallization, dielectric surface, copper, reaction, coating, films.

Introduction

Decomposition of copper halides and their analogs under the influence of light refers to the photochemical method. At the same time, part of the sample exposed to brightened, and particles of copper, gold and silver are formed on the surface.

When processing the surface layer of the material under the influence of solar treatment with CuCl solution, a black layer gradually forms on the surface of the fabric. The reaction is characterized by the following equation:

$$2CuCl \xrightarrow{h\nu} Cu + CuCl_2 \quad (1)$$

When processing the surface of the material is treated with a solution of CuCl, both of these reactions occur on the surface of the fabric and form solid crystals of chlorine copper. Crystals can be rinsed with water, but when added to the water, the black coating of the copper is lost, which indicates the return reaction:

$$Cu + CuCl_2 \rightarrow 2CuCl \quad (2)$$

To obtain high-quality coatings on the surface of dielectric materials and to study their physicomechanical properties, it is necessary to study the mechanism of photochemical reduction of copper coatings and its substrate.

It is known that most unipolar compounds of a copper substrate decompose quickly under the influence of heating or light. It is also known that metal halogenates of a copper substrate are binary semiconductors. Therefore, there is a relationship between semiconductor properties and photosensitivity.

The sensitivity of halides is used to produce metal layers on these surfaces to give them bactericidal properties. Such products may include door handles, fire extinguishers, curtains, pillows, dressings, bactericidal impregnations in household appliances, clothing [1].

Since ancient times, mankind has known about the bactericidal properties of copper and its analogues. In 2008, the status of substances with a bactericidal surface of copper and its several melts was officially given. There is a tendency to use silver, as well as copper, in the production of bactericidal coatings [2, 3].

Thus, the method of laying metal coatings of copper substrate on different surfaces is widely used in different fields of technology. In particular, the use of bactericidal properties of copper and its analogues in medical materials is promising. It is convenient to use copper (II) chloride and gold (III) chloride when removing the light fluidized chloride layer. Therefore, the proposed work provides a mechanism for the transformation of light-sensitive coatings on various materials of these salts [4].

Results and Discussion

Cotton fabric was used in the studies (marking AA010278), which is most widely used for medical purposes [5]. Separate experiments on the photochemical reduction of copper halides were carried out in monovalent copper solutions. Thus, a suspension of 30 g of CuCl in 100 ml of water was prepared to obtain a copper coating on the surface of the fabric material, and then the solution was poured onto the surface of the fabric. Next, the sample is exposed to sunlight. Depending on the drying of the fabric, its surface is covered with a black layer. Covered areas with light-resistant protection remain unchanged in accordance with Figure 1.

Two products obtained by reaction 1 stay on the surface of the fabric as solid crystals of copper di-chloride and nanoparticles of copper. However, the black layer of copper is eliminated by the addition of water, which means a backlash 2.

The correctness of this mechanism is confirmed by experiments on photochemical reactions on the surface of copper samples. In the following experiments, the samples were treated with copper (II) bromide. In this case, the halide compounds react with the copper surface to the following reaction:

$$CuBr_2 + Cu \rightarrow 2CuBr \quad (3)$$

When the surface is immediately exposed to sunlight after such treatment, its surface layer is colored. In addition, the dark color of the sample depends on its drying. In addition, some areas of the sample were darkened from sunlight when they were exposed to the sun. Figure 2 shows the color change of the copper sample at each stage of the process [6].

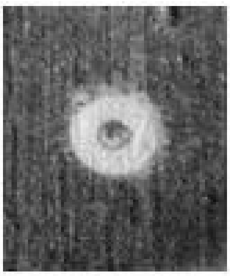
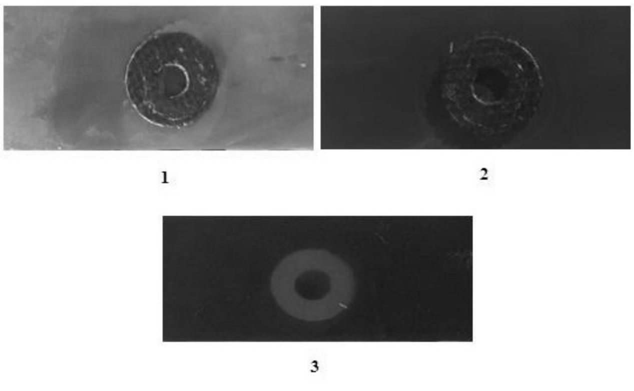


Figure 1. The fabric is treated with an aqueous solution of CuCl and exposed to sunlight



1 — surface layer after treatment in a solution of 30 g/l $CuCl_2$; *2* — sample surface treatment after exposure to sunlight; *3* — surface layer after screening of some parts under the influence of solar treatment

Figure 2. Changing the color of surfaces in samples during exposure to a light-sensitive layer

Consequently, the copper base, which is a reducing agent, contributes to the slowing down of the reaction. Therefore, it is recommended that the sodium hypophosphite solution be added to the solution by coppering dielectric materials.

Methods of copper coating were carried out in fabric samples measuring 2×5 cm to determine the individual technological parameters of the process. The sample is poured with a solution of $CuCl_2 \times 2H_2O$ —

100 g/l. In this connection, the volume of the solution retained by the sample was 0.6 ml. Copper in this solution is about 25×10^{-3} g [7].

The results of the study revealed that the process of photochemical reduction of copper consists of two stages: the formation of a semiconductor layer due to an increase in the concentration of halogen during the drying of the coating occurs in the first 30 minutes of the first stage. Direct photochemical reduction of copper, which takes about 30 minutes, but then gradually slows down in the second stage. Therefore, in the second stage, the rate of the photochemical reaction is equal to the rate of chemical or galvanic metallization.

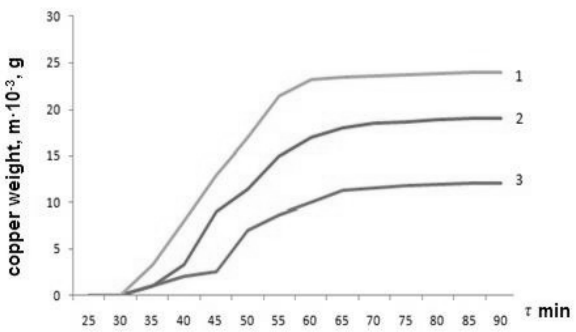
The following empirical relationships were obtained for studying the reaction kinetics mechanism. The influence of the concentration of copper chloride on composite copper and its analogs has been studied. As shown in Table 1, the concentration of copper chloride increases with the weight of the coating, but the thickness of the coating does not affect the absorption rate of copper chloride in accordance with Figures 3–5. Consequently, the reaction rate of copper chloride is 0.

Table 1

Effect of copper chloride concentration on the weight of the film

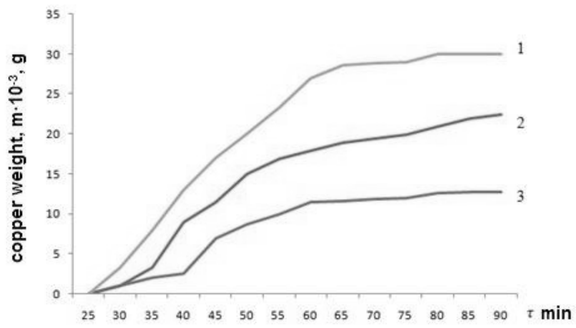
Weight of copper, mg	Time, min	Concentration of copper chloride, g/l							
	0–30 min	0.1	1	10	30	50	70	100	150
		0.024	0.24	2.4	7.2	12	16.8	24	36

The reaction rate of copper chloride at various concentrations (differential method) was studied in accordance with Figures 6–8.



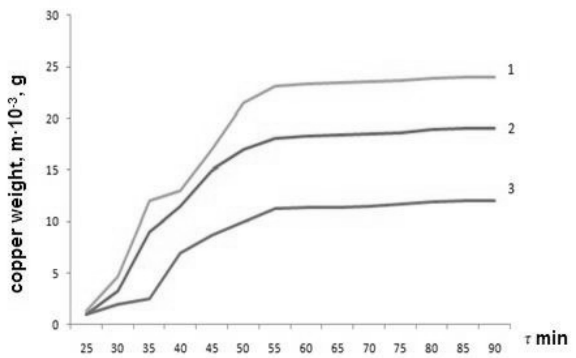
1 — 200 g/l; *2* — 100 g/l; *3* — 50 g/l

Figure 3. The rate of reduction of copper (II) chloride under sunlight at 25 ºC



1 — 200 g/l; *2* — 100 g/l; *3* — 50 g/l

Figure 4. The rate of reduction of copper (II) chloride under sunlight at 35 ºC



1 — 200 g/l; *2* — 100 g/l; *3* — 50 g/l

Figure 5. The rate of reduction of copper (II) chloride under sunlight at 40 ºC

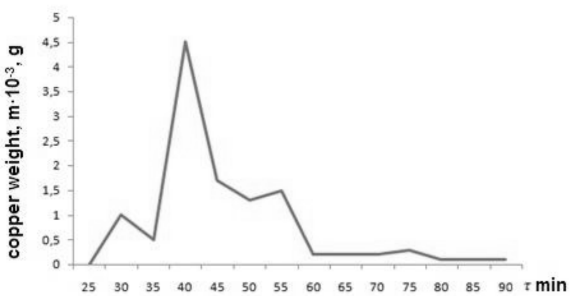


Figure 6. Recovery rate of copper chloride at a concentration of 50 g/l under the influence of sunlight

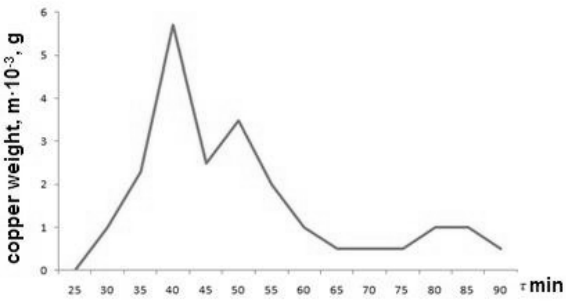


Figure 7. Recovery rate of copper chloride at a concentration of 100 g/l under the influence of sunlight

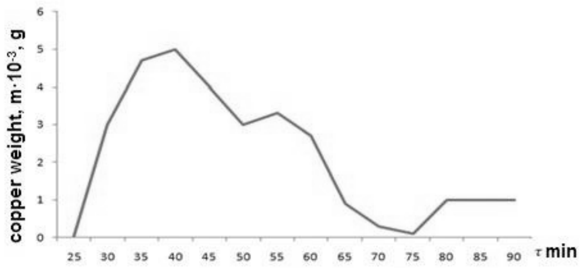


Figure 8. Recovery rate of copper chloride at a concentration of 150 g/l under the influence of sunlight

The reaction rate was studied at different concentrations of copper chloride to determine the order of the reaction.

$$2CuCl_2 + H_2O + NaH_2PO_2 \rightarrow 2CuCl + 2HCl + NaH_2PO_3 \quad (4)$$

The reaction rate is calculated by the Vant-Hoff method (differential method) using the following formula:

$$n_i = (\lg W_1 - \lg W_2) / (\lg C_{0.1} - \lg C_{0.2}). \quad (1)$$

Description: W_1, W_2, $C_{0.1}$ and $C_{0.2}$ actual rates of reaction at baseline concentrations; n_i — the concentration is C_0 individually in the component.

The results are shown in Table 2.

Table 2

Effect of copper chloride concentration on the rate and order of the reaction

Concentration of copper chloride, mol/l·10^{-3}	4.5	5.8	5
Actual reaction rate, l/min·10^3	0.112	0.145	0.125
Reaction order	-	0.365	0.365

The reaction rate does not affect the moisture content of the mixture (i.e. H_2O). Let's calculate the true reaction rate:

$$W_1 = 4.5/40 = 0.112;$$

$$W_2 = 5.8/40 = 0.145;$$

$$W_3 = 5/40 = 0.125.$$

$$n_1 = (\lg W_1 - \lg W_2) / (\lg C_{0.1} - \lg W_{0.2}). \quad (2)$$

$$n_1 = \frac{0.653 - 0.763}{-1 - (-0.698)} = \frac{-0.110}{-0.301} = 0.365.$$

$$n_2 = (\lg W_2 - \lg W_3) / (\lg C_{0.2} - \lg W_{0.3}). \quad (3)$$

$$n_2 = \frac{-0.838 - (-0.903)}{-0.698 - (-0.522)} = \frac{0.064}{0.176} = 0.365.$$

Thus, the kinetic equation for the complete reaction for the formation of composite shells of copper and its analogs is written as follows:

$$V = K \cdot C^{0.366-0.365}. \quad (4)$$

Description: k — reaction rate constant, min $^{-1}$.

The following formula is used to determine the activation energy:

$$E_{act} = \frac{RT_1T_2 \lg\left(\frac{K_{T1}}{K_{T2}}\right)}{T_2 - T_1}. \quad (5)$$

Description: E_{act} — activation energy of the reaction, J/mol.

$$0.1125 = k_1 \cdot 4.5^{0.366};$$

$$k_1 = \frac{0.112}{1.73} = 0.065;$$

$$0.145 = k_2 \cdot 5.8^{0.366};$$

$$k_2 = \frac{0.145}{1.190} = 1.218;$$

$$0.125 = k_3 \cdot 5^{0.366};$$

$$k_3 = \frac{0.125}{1.801} = 0.069.$$

Activation energy:

$$E_{act} = \frac{RT_1T_2 \lg\left(\frac{K_{T1}}{K_{T2}}\right)}{T_2 - T_1}. \quad (6)$$

Well, then,

$$E_{act1} = \frac{2.303 \cdot 8.31 \cdot 298 \cdot 308\left(0.064/1.218\right)}{(308-298)} = \frac{0.053 \cdot 308 \cdot 298 \cdot 8.31 \cdot 2.303}{10} = 9.437 \cdot 10^3;$$

$$E_{act2} = \frac{2.303 \cdot 8.31 \cdot 298 \cdot 313\left(0.069/1.218\right)}{(313-298)} = \frac{0.053 \cdot 308 \cdot 298 \cdot 8.31 \cdot 2.303}{10} = 6.762 \cdot 10^3.$$

The results of the study of the temperature dependence of the reaction rates in time are given in Table 3. Consequently, a low concentration of the coating formation makes it possible to obtain a semigloss coating, which varies from black to gray-black. The coating thickness was about 0.3–0.6 μm, depending on the concentration of copper chloride, the base material and the surface layer. Thus, as a result of photochemical reaction of the sorption layer under the influence of sunlight, copper semiconductors form metal coatings on the surface. This, in turn, can be used to produce thinner coatings.

Table 3

The influence of time and temperature on the reaction rate and its constant

Parameters	Temperature, ºC	Time, min (40 min)
Rate of reaction, sm^3/min	308 298 313	0.112 0.145 0.125
Rate constant, min^{-1}	308 298 313	0.064 0.218 0.069
Activation energy, J/mol		9.437×10^3 6.762×10^3

Conclusions

Mechanisms of photochemical reactions in thin layers of solutions of copper halide are presented. Copper halides and its analogs can participate in the oxidation-reduction reaction under the influence of sunlight. In thin films, monovalent halides are formed first under the action of beams. These are semiconductors, because they are oxidized by the sun's quantum of light, and the positive charge generated at this moment is the «vacancies» of the water molecule or oxidizes the hydroxide layers of material cellulose.

As a result of photochemical reaction in the sorption layer under the influence of sunlight it is proved that semiconductor copper components forming metal coatings on the surface are formed. It is shown that the process of studying the photochemical reduction of copper is two steps.

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Диэлектрлік беттерді фотохимиялық металдау процесінің механизмі

Мақалада мысқұрамдас қаптамаларды әртүрлі үлгілердің бетіне қондыру мүмкіндігі зерттелген. Зерттеу үшін тегіс және жалпақ мыс пластиналар мен мата қолданылды. Диэлектрлі материалдың үлгісі ерітіндіге батырылды, олар күн энергиясымен кептірілді және мыс үлгінің бетіне тұндыру бойынша жұмыс жүргізілді. Мыстың фотохимиялық тотықсыздану жылдамдығын зерттеу процесі екі кезеңнен тұрады. Бірінші кезеңнің алғашқы 30 минуты — бұл қаптаманы кептіру кезінде галогендердің концентрациясын арттыру есебінен жартылайөткізгіш қабаттың қалыптасуы, ал екіншісі — 30 минутқа жуық уақыт алатын мыстың тікелей фотохимиялық тотықсыздануы, бірақ содан кейін біртіндеп баяулайды. Екінші кезеңде фотохимиялық реакция жылдамдығы химиялық немесе гальваникалық метализация жылдамдығына тең. Фотохимиялық реакция нәтижесінде күн сәулесінің әсерінен сорбциялық қабат құрғаған кезде бетінде металл қаптаманы құрайтын мысты жартылайөткізгіштер пайда болады. Бұны, өз кезегінде, жұқа қаптамаларды дайындау үшін пайдалануға болады.

Кілт сөздер: механизм, фотохимия, метализация, диэлектрлік бет, мыс, рекция, қаптама, қабат.

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Механизм процесса фотохимической металлизации диэлектрических поверхностей

В статье исследована возможность нанесения медьсодержащих покрытий на поверхности различных образцов. Для исследования были использованы плоские и гладкие медные пластины и ткань. Образец диэлектрического материала был погружен в раствор, затем они были высушены на солнце, и была проделана работа по осаждению меди на поверхность образца. Изучение скорости фотохимического восстановления меди показывает, что процесс состоит из двух этапов. В первые 30 минут первого этапа за счет увеличения концентрации галогенов при сушке покрытия образуется полупроводниковый слой, а во второй — прямое фотохимическое восстановление меди, которое занимает около 30 минут, но затем постепенно замедляется. На втором этапе скорость фотохимической реакции равна скорости химической или гальванической металлизации. В результате фотохимической реакции при высыхании сорбционного слоя под воздействием солнечных лучей на поверхности образуются медные полупроводники, формирующие металлическую пленку.

Ключевые слова: механизм, фотохимия, металлизация, диэлектрическая поверхность, медь, реакция, покрытие, пленки.

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